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A GENERAL SYNTHESIS FOR DITUNGSTEN TETRACARBOXYLATES
PREPARATION OF W-W Q. (U) INDIANA UNIV AT BLOOMINGTON
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A GENERAL SYNTHESIS FOR DITUNGSTEN TETRACARBOXYLATES.
PREPARATION OF W-W QUADRUPLE BONDS BY REDUCTIVE-ELIMINATION
(ALKYL GROUP DISPROPORTIONATION) FROM 1,2-DIETHYL COMPOUNDS
WITH W-W TRIPLE BONDS.

by

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) dinuclear reductive-elimination, tungsten, quadruple bonds, carboxylates		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → A general high yield synthesis for $W_2(O_2CR)_4$ compounds is proposed based on eq. 1, wherein a W-W triple bond is converted to a quadruple bond, and this has been established for R = Me, Et and t-Bu. 1 $W_2Et_2(NMe_2)_4 + 4RCOOCOR \longrightarrow W_2(O_2CR)_4 + 4RCONMe_2 + C_2H_4 + C_2H_6$		

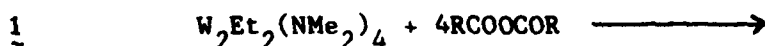
A General Synthesis for Ditungsten Tetracarboxylates.

Preparation of W-W Quadruple Bonds by Reductive-Elimination (Alkyl Group Disproportionation) from 1,2-Diethyl Compounds with W-W Triple Bonds.

The search for compounds containing W-W quadruple bonds, particularly ditungsten tetracarboxylates, is one of the fascinating stories in the development of the chemistry of compounds containing multiple bonds between metal atoms.^{1,2} At this time there are two reports of the preparation and characterization of $W_2(O_2CR)_4$ compounds. Sattelberger and McLaughlin³ reported in 1981 that reduction of $W_2Cl_6(THF)_4$ with 2 equivalents of sodium amalgam in THF at $-20^\circ C$, followed by addition of sodium trifluoroacetate (4 equiv) gave, upon work up, $W_2(O_2CCF_3)_4$ in 20% yield based on tungsten. More recently Cotton and Wang⁴ reported a higher yield synthesis (ca. 55% based on W) for the benzoate, $W_2(O_2CPh)_4 \cdot 2THF$, from Na/Hg reduction of WCl_4 in THF followed by treatment with sodium benzoate. We wish here to report a general high yield synthesis for $W_2(O_2CR)_4$ (MEM) compounds based on reductive elimination (alkyl group disproportionation) from $W \equiv W$ containing compounds.

Hydrocarbon solutions of $1,2-W_2Et_2(NMe_2)_4$ ⁵ react quickly at room temperature with acid anhydrides $RCOOCOR$, where $R = Me, Et$ and $t-Bu$, according to equation 1. These reactions appear quantitative when they are carried out in sealed nmr tubes and followed by 1H nmr spectroscopy. In the absence of oxygen donor solvents, the tetracarboxylates are isolated either as weakly ligated polymers $[W_2(O_2CR)_4]_n$, where $R = Me$ or Et ⁶, as shown in Figure 1, or as the $RCONMe_2$ adduct $W_2(O_2C-t-Bu)_4 \cdot 2t-BuCONMe_2$, by crystallization from benzene or hexane. These

new compounds are bright yellow, crystalline, volatile, air-sensitive compounds and appear analogous to the two previously reported related compounds. An extension of eq. 1 to include other R groups seems obvious.



The present finding is of interest and worthy of note because it reveals that by appropriate synthetic strategy W-W triple bonds can be converted to W-W quadruple bonds.⁷ This is the first observation of this transformation.



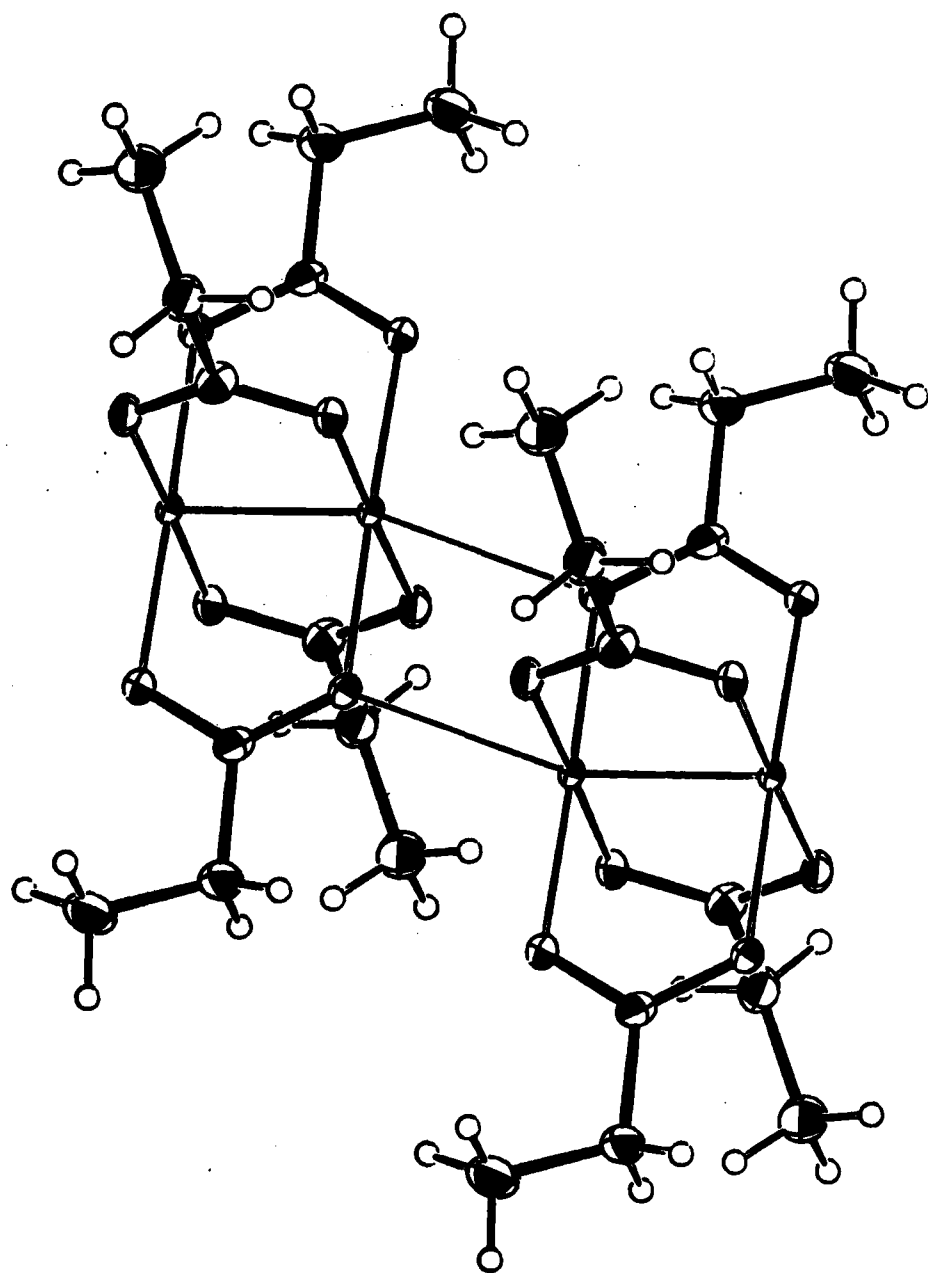
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6. Crystal data for $W_2(O_2CET)_4$ at $-160^\circ C$: $a = 9.377(2)\text{\AA}$, $b = 8.271(2)\text{\AA}$, $c = 5.527(1)\text{\AA}$, $\alpha = 102.49^\circ$, $\beta = 84.61(1)^\circ$, $\gamma = 89.45(2)^\circ$, $Z = 1$, $d_{\text{calcd}} = 2.631\text{gcm}^{-3}$ and space group $P\bar{1}$. Data collection was performed using standard moving crystal-moving detector techniques (MoK α $6^\circ < 2\theta < 50^\circ$). Of 1477 unique intensities, 1464 having $F > 2.33\sigma$ (F) were used in the refinement. The W atom position was located in a Patterson and all remaining atoms, including H atoms, were located in the Fourier synthesis. A final difference Fourier was featureless, the largest peak being $0.83\text{e}/\text{\AA}^3$, located near the W position. Final residuals are $R(F) = 0.016$ and $R_w(F) = 0.015$.
7. Reactions between $W_2Et_2(NMe_2)_4$ and each of CO_2 and $ArNNNHAr$ do not appear to parallel reactions wherein Mo-Mo triple bonds are converted to Mo-Mo quadruple bonds. These reactions are under continuing investigation: Chetcuti, J.J.; Chisholm, M.H.; Folting, K., Haitko, D.A., Huffman, J.C. J. Am. Soc. 1982, 104, 2138.

Caption to Figure 1

An ORTEP view of the centrosymmetric $W_2(O_2C\text{Et})_4$ molecule showing the connectivity in the infinite chain $[W_2(O_2C\text{Et})_4]_n$. Pertinent distances (Å) and angles ($^\circ$) (averaged where appropriate), are W-W = 2.189(1), W-O = 2.08(2), W---O = 2.665(4), W-W-O = 91(1), W-W---O = 161.6(1). $^\circ$



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